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Structure and bonding in some organotitanium and related compounds

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S U M M A R Y

In this thesis investigations on the structure and chemical bonding in some organometallic compounds of transition metals with few d electrons are described. Structural studies involve the X-ray diffraction analyses of two titanium compounds. Theoretical studies deal with the electronic structure of sandwich compounds based on self-consistent field (SCF) MO calculations using two different theoretical models.

In Chapter I the stabilization of electron-deficient 3d metallocenes, $(C_5H_5)_2M$, upon coordination of additional ligands is discussed on the basis of qualitative MO considerations. Replacement of a C_5H_5 group by a larger organic ring system, e.g. C_7H_7 , may also lead to a stable sandwich compound.

Chapter II deals with the structure of the titanium-dinitrogen complex $[(C_5H_5)_2Ti(p-CH_3C_6H_4)]_2N_2$. The binuclear molecule consists of two $(C_5H_5)_2Ti(p-CH_3C_6H_4)$ entities bridged by the dinitrogen ligand in an essentially linear manner. The titanium atoms have a pseudo-tetrahedral environment. The cyclopentadienyl rings are π bonded to the Ti atoms; the ring planes are mutually inclined at an angle of 43° . The aryl groups are σ bonded to the Ti atoms and are coplanar with the linear TiN_2Ti unit within 0.12 \AA . The dinitrogen ligand exhibits a significantly longer N-N distance ($1.162(12) \text{ \AA}$) than that of free N_2 (1.0976 \AA), indicative of a substantial reduction in N-N bond order. The relationship between the structure and the chemical reactivity of the dinitrogen ligand is discussed. A qualitative picture of the titanium-dinitrogen bonding is presented.

The structure determination of $(C_5H_5)Ti(C_7H_7)$, described in Chapter III, confirms the sandwich structure of this compound. An interesting structural feature are the unusually short Ti-C bond distances in the $Ti(C_7H_7)$ moiety (2.19 \AA). In addition, this chapter presents a survey of the experimental investigations on the charge distribution in $(C_5H_5)Ti(C_7H_7)$ and the corresponding vanadium and chromium compounds. A discussion of the considerations leading to the theoretical calculations on these molecules is also given.

In Chapter IV the Hartree-Fock (HF) and Hartree-Fock-Slater (HFS) methods are reviewed. The application of the two methods to the compounds $(C_5H_5)M(C_7H_7)$ with $M = Ti, V, \text{ and } Cr$ is described in Chapters V and VI.

In Chapter V-part 1 HF-LCAO calculations with small basis sets of Gaussian-type orbitals are described for the ground-state molecules. Basis-set effects have been investigated by means of calculations with different basis sets on the free metals, the free rings, and the moieties $(C_nH_n)_M$ ($n = 5,7$). These calculations indicate that the near minimum basis-set results provide a reasonable basis for a discussion of the trends in the charge distributions of the mixed sandwich compounds. Within the framework of Mulliken's population analysis it is shown that the negative charge on the C_7H_7 ring decreases in the order Ti, V, and Cr, while the negative charge on the C_5H_5 ring increases in this order. Details of bonding are discussed. The overall picture concerning the trends in bonding and gross charges can be summarized in simple terms. The observed trends in metal 2p and 3s and carbon 1s ionization energies are quite well reproduced by the corresponding ground-state orbital energies.

In Chapter V-part 2 HFS-LCAO calculations with fairly large basis sets of Slater-type orbitals are described for the ground-state molecules $(C_5H_5)_M(C_7H_7)$. Population analyses show that the negative charge on the C_7H_7 ring rapidly decreases from Ti to Cr. The negative charge on the C_5H_5 ring also decreases in this sequence but less pronounced. These trends are in accord with the experimental findings concerning the charge distributions in the three compounds. An analysis of the charge distribution in terms of the free-metal and free-ring orbitals reveals that the metal effectively acts as a strong δ -electron donor towards C_7H_7 and as a moderate π -electron donor towards C_5H_5 . The trend of decreasing donation with atomic number of the metal is rationalized on the basis of molecular orbital interaction diagrams at the HFS level. An analysis is made of the various contributions to the binding energies.

Chapter VI mainly deals with independent SCF calculations on a number of electronic configurations of the positive ions $[(C_5H_5)_M(C_7H_7)]^+$. The dominant feature of the valence ionizations within both HF and HFS frameworks is the large reorganization of the charge distributions in all cases considered. The corresponding relaxation energies obtained by the HF- Δ SCF method depend strongly on the amount of metal character of the ionized ground-state orbitals. The trends in the calculated ionization energies as a function of the metal agree only partly with those derived from the observed photoelectron spectra.

Finally, in this chapter the ultraviolet and visible absorption spectra of the mixed sandwich compounds are reported, together with some electronic transition energies calculated by the HFS transition-state method. The agreement of the calculated excitation energies with experiment is satisfactory.

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